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BASE INDUCED, INTRAMOLECULAR CYCLIZATION WITH OXIDATION IN 9-DIALKYLAMINO-1-ALKYLAMINO-PHENALENIUM IONS[1)]

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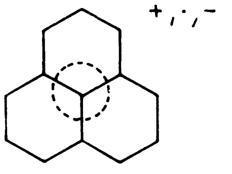
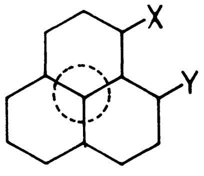
Alkylation of 9-methylamino-1-methyliminophenalene, (1), gives 1,9-disubstituted phenalenium salts, (2a,b), which can be cyclized to (4a,b) in the presence of amine and oxygen forming a new N-C bond. A possible mechanism with a Mannich Base type intermediate is discussed. The structure of the new compounds is deduced from their ^{1}H- and ^{13}C-NMR spectra.

The 13-membered carbocycle phenalenyl, A, has three stable oxidation states (+1,0,-1),[2)] and retains this property in many of its derivatives.[3)] In particular, 1,9-disubstituted phenalenes, B, can be oxidized and reduced chemically and electrochemically.[4)] The carbon skeleton occurs in several natural organic substances and also in a compound with mutagenic activity.[5)] The property of stabilizing positive and negative charge makes it of interest for its behaviour in charge-transfer complexes[6)] and - as outlined below - influences also its reactivity.



A



B

X,Y = OR, SR, RNR'

During an investigation of nucleophilic substitution on phenalenium systems, we prepared compounds (2a,b) by alkylation of (1) with $((CH_3)_3O)^+BF_4^-$ or $((CH_3CH_2)_3O)^+BF_4^-$ respectively.[7)] Treatment of a solution of (2a,b) in CH_3CN with CH_3NH_2 (30% in ethanol) and addition of n-heptane gives a purple precipitate (ca. 60%) which can be recrystallized from chloroform, (4a) m.p. 223°C, λ_{max}(nm) ($\varepsilon \times 10^3$): 535(5.63), 387(29.18), 259(30.18); (4b), m.p. 236°C, λ_{max}(nm) ($\varepsilon \times 10^3$): 534(7.84), 390(34.56), 260(37.92); in CH_3CN. The new compounds are stable in air and dissolve in water and organic solvents without decomposition. The reaction is independent of both the base used and of the counterion (e.g. $(CH_3)_2NH$ (30% in ethanol) and $((CH_3)_3O)^+PF_6^-$).

TABLE. ^1H (δ_{TMS}) and ^{13}C (ppm_{TMS}) NMR resonances for (4a) and (4b), CD_3CN [12)]

		1	2	3	4	5	3a	9a	9b	CH_3	CH	R
(4a)	^1H	-	7.24	8.28	8.16	7.64	-	-	-	3.28	5.24	5.24
	^{13}C		116.5	144.4	137.4	126.8				38.3	69.9	-
(4b)	^1H	-	7.14	8.20	8.08	7.60	-	-	-	3.28	5.50	1.38
	^{13}C	152.5	117.0	144.2	137.0	126.6	126.6	125.7	106.4	38.2	77.1	14.7

^1H- and ^{13}C-NMR spectra (see Table) are consistent with structures (4a,b) for the products. The mass spectra of (4a) and (4b) show parent ions.

The ^1H-NMR spectrum of (4b), Figure 1, indicates an axis of symmetry along C_5-C_{9a} for the ring protons,[8)] and two equivalent methyl groups at δ = 3.28 (CD_3CN, TMS_i). There is also a well-resolved quartet for one proton which is coupled (J = 6 Hz) to a doublet of three protons at δ = 1.38. The ^{13}C-NMR spectrum shows two single and two equivalent carbon signals in addition to the ring resonances. Coupling with ^1H produces one doublet (J_{CH} = 36.88 Hz) and two quartets ($J_{(CH_3)_2}$ = 37.19 Hz; J_{CH_3} = 29.30 Hz).

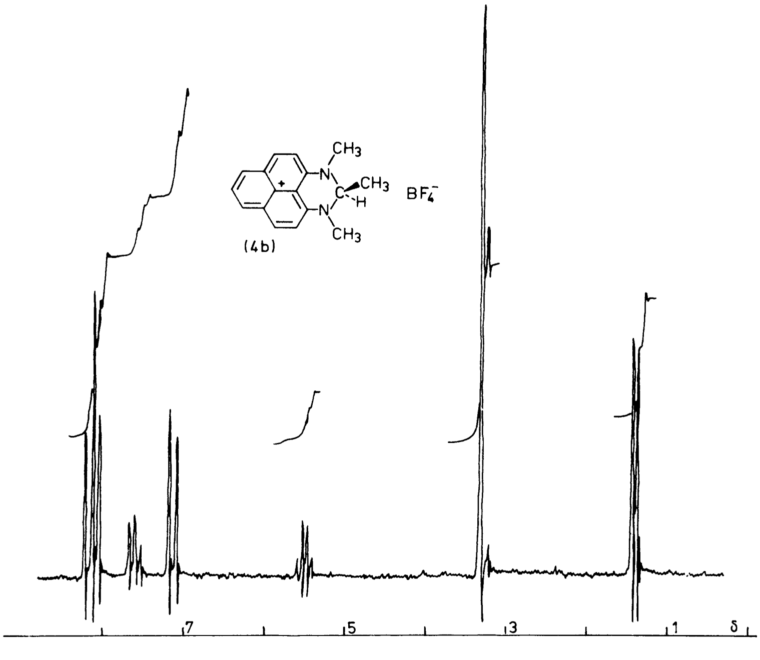


Figure 1 ^1H NMR spectrum of (4b).

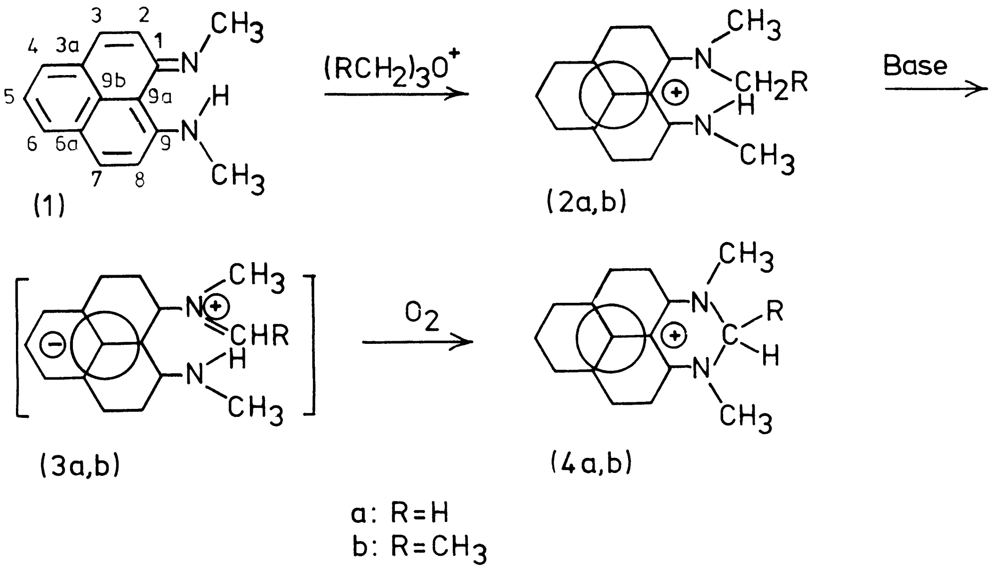


Figure 2: Reaction scheme and proposed intermediate, (3), for the intramolecular cyclization.

The NMR results for (4a) are also consistent with the above interpretation. Assignment of the ^{13}C ring resonances is possible by comparison with other cationic phenalene derivatives where a reasonable correlation exists between calculated charge densities and chemical shifts.[9)]

A likely mechanism for the reaction is indicated in Figure 2. In contrast with 1,9-dialkoxyphenalene cations,[4)] the substituents are not exchanged by primary or secondary amines and the composition of the products (4a,b) is independent of the base. Deprotonation of (2a,b) leads to a neutral intermediate (3a,b) with a Mannich Base like substituent $>\overset{+}{N}=CHR \Leftrightarrow >\overset{-}{N}-\overset{+}{C}HR$. The positive charge can be stabilized within the molecule by the phenalenyl system as discussed above. The rigid framework of the ring system brings the electrophilic end of the Mannich Base[10)] close to the nucleophilic amine. The cyclic product (4a,b) is then formed by air-oxidation with loss of the N-bound hydrogen.[11)]

It is not quite understood so far, why the reaction of (2b) yields only one product, (4b). The other possible isomer did not show up in the ^{1}H-NMR spectrum of the crude product.

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12) The solubility of (4a) was too low to assign carbon nucleii with low relaxation times. (1, 3a, 9a, 9b).

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